

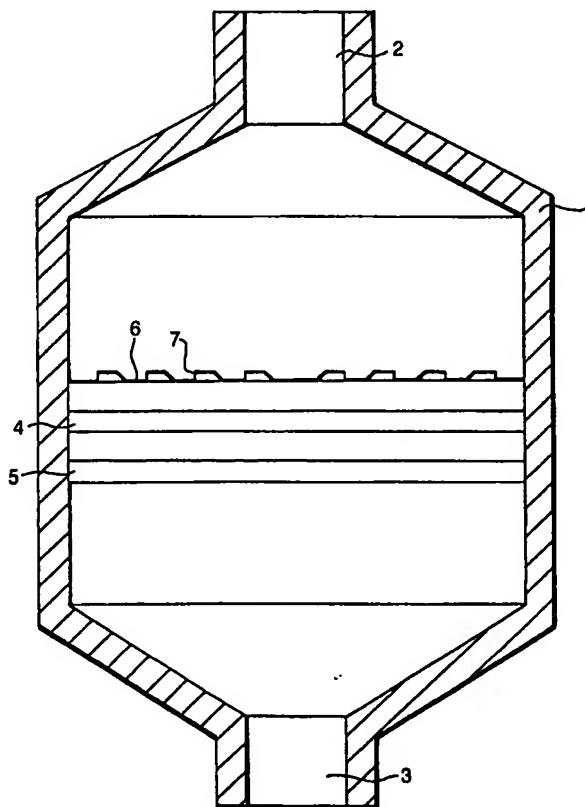
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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/GB98/01649 <b>(22) International Filing Date:</b> 4 June 1998 (04.06.98)  <b>(30) Priority Data:</b> 9712444.0 17 June 1997 (17.06.97) GB  <b>(71) Applicant (for all designated States except US):</b> IMPERIAL CHEMICAL INDUSTRIES PLC [GB/GB]; Imperial Chemical House, Millbank, London SW1P 3JF (GB).  <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> SHIPLEY, David, Graham [GB/GB]; 12 Fir Tree Close, Hilton, Yarm, Cleveland TS15 9JZ (GB).  <b>(74) Agents:</b> GRATWICK, Christopher et al.; ICI Group Intellectual Property, P.O. Box 90, Wilton, Cleveland TS90 8JE (GB).		<b>(81) Designated States:</b> AU, BR, CA, CN, CZ, GE, HU, ID, JP, KR, MX, NO, NZ, PL, RO, SK, UA, US, UZ, Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>

**(54) Title:** AMMONIA OXIDATION**(57) Abstract**

In order to render the catalyst temperature more uniform in a catalytic ammonia oxidation process, the preheated reactants mixture, i.e. ammonia and oxygen-containing gas, is passed through a perforate reflector disposed upstream of the catalyst bed, said reflector being effective to reflect heat radiated from the inlet face of the catalyst bed back towards the catalyst bed.



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Ammonia oxidation.

This invention relates to ammonia oxidation. Ammonia oxidation is widely employed in the manufacture of nitric acid and hydrogen cyanide. In the manufacture of nitric acid ammonia is oxidised with air to nitric oxide, while in the manufacture of hydrogen cyanide a mixture of ammonia and methane (often as natural gas) is oxidised with air. In both processes, the gas mixture is passed at an elevated temperature over a catalyst to effect the oxidation. Side reactions, such as the formation of nitrogen or nitrous oxide, are undesirable. Consequently, in addition to good activity, the catalyst is required to have a good selectivity.

The oxidation reaction is exothermic: as the heated gas mixture passes through the catalyst, the oxidation reaction proceeds with the evolution of heat, causing the temperature of both the gas mixture and the catalyst to increase until a steady state condition is reached. The selectivity of the reaction depends on the catalyst temperature, and for any given operating conditions, i.e. gas composition, catalyst, catalyst age, flow rate etc. there is generally an optimum temperature. The catalyst temperature may be controlled by modification of one or more of the process variables, for example the temperature to which the gas mixture is pre-heated and/or the proportion of ammonia in the gas mixture.

We have noticed however that there is liable to be a significant temperature gradient through the catalyst and so not all the catalyst is operating at the desired optimum. In part this temperature gradient results from radiation of heat from the inlet side of the catalyst into the incoming gas mixture.

In the present invention the effect of such radiation is minimised.

Accordingly the present invention provides for the oxidation of ammonia comprising passing a mixture of ammonia and an oxygen containing gas preheated to an elevated temperature through at least one bed of a catalyst effective for the oxidation of ammonia wherein, in order to render the catalyst temperature more uniform, the gas mixture is passed through a perforate reflector disposed upstream of the catalyst bed, said reflector being effective to reflect heat radiated from the inlet face of the catalyst bed back towards the catalyst bed.

The catalyst may be platinum, optionally alloyed with other precious metals such as rhodium, in the form of meshes or gauzes formed from the metal wire. Alternatively the catalyst may be in the form of pellets, extrudates or granules of an oxidic material such as a composition containing cobalt oxide. For example, it has been proposed in CN-A-86 108 985 to employ lanthana/ceria/cobalt oxide compositions of the general formula  $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$  (where x is from 0 to 1) made by a specified co-precipitation route as ammonia oxidation catalysts. Oxidic catalysts preferably contain at least one mixed oxide phase containing cobalt and at least one element A selected from rare earths and yttrium, said cobalt and element A being in such proportions that the element A to cobalt atomic ratio is in the range 0.8 to 1.2, particularly 1.0 to 1.2. Preferably at least

one element selected from yttrium, cerium, lanthanum, neodymium, and praseodymium is used as part or all of element A. Element A may comprise a mixture of at least one variable valency element Vv selected from cerium and praseodymium and at least one non-variable valency element Vn selected from yttrium and the non-variable valency rare earth elements such as lanthanum or neodymium. In particular it is preferred that the atomic proportions of variable valency element Vv to non-variable valency element Vn is in the range 0 to 1, particularly 0 to 0.3. Such oxidic catalysts may be in a form wherein the amount of oxygen is non-stoichiometric. This arises from the variable valency of cobalt and also of any variable valency rare earth present as part, or all, of element A.

In the process of the invention, a radiation reflector is disposed upstream of the catalyst to reflect heat radiated from the inlet face of the catalyst back to the catalyst. In this way heat loss from the inlet face of the catalyst is minimised and so the catalyst temperature is more uniform. The reflector is preferably a perforate plate disposed just upstream of the catalyst. The perforations should be of sufficient number and size that the reflector presents only an insignificant impedance to the flow of the gas mixture therethrough, but, on the other hand they should only form a minor proportion of the area of the reflector so that a substantial amount of the radiation is reflected. Preferably the perforations are in the form of louvres so that essentially all the area of the reflector acts to reflect the radiated heat. The reflector may also act as a diffuser to ensure even distribution of the gas mixture through the catalyst bed. The reflector is preferably positioned between 1 and 30 cm above the top of the catalyst bed.

The invention is illustrated by reference to the accompanying drawings wherein Figure 1 is a diagrammatic cross section of an ammonia oxidation reactor. Figure 2 shows an alternative arrangement.

In Figure 1 there is shown a vessel 1 having an inlet port 2 and an outlet port 3. Disposed across the vessel are catalyst beds 4, 5 each composed of a wad of gauzes formed from a platinum/rhodium alloy wire. Upstream of the bed 4 nearest the inlet port is disposed a reflector plate 6 formed from a suitable heat resistant metal such as Incalloy. A plurality of louvres 7 are provided in the reflector plate 6.

In use a mixture of ammonia and air, preheated to a desired inlet temperature, is fed to the inlet port 2. The mixture passes through louvres 7 in the reflector plate and then through the catalyst beds 4 and 5. Oxidation of the ammonia occurs with the evolution of heat. As a result the temperature of the both the catalyst and the gas mixture increases. The reacted gas then leaves the reactor via outlet port 3. Under steady state operation the temperature of the catalyst bed 5 and the reacted gas are essentially the same. Likewise the temperature through most of the thickness of the catalyst bed 4 is the same as that of the reacted gas mixture. However heat is liable to be lost from the inlet, i.e. upper, face of catalyst bed 4 by radiation into the incoming gas stream. A substantial amount of this radiated heat is reflected back towards the catalyst bed 4 by the reflector

plate 6, thereby reducing the temperature difference between the inlet portion of the catalyst bed 4 and the remainder of the catalyst bed. In this was the temperature of the catalyst bed is more uniform enabling the reaction conditions to be selected to give the optimum selectivity.

5 An alternative arrangement is shown in Figure 2. Here the reflector consists of a pair of metal plates 8, 9 spaced one above the other. Each plate is perforate so as to allow passage of the reactants through the plates, but the perforations are staggered so that heat radiated from the catalyst bed passing through the perforations of the lower plate is reflected by the lower surface of the upper plate.

10 In some cases it may be desirable to provide a layer of thermal insulation on the upper surface of the reflector, i.e. on the surface remote from the catalyst bed, to minimise heat loss from the upper surface of the reflector.

In the oxidation of ammonia to nitric oxide for the manufacture of nitric acid, the oxidation process may be operated at temperatures of 800-1000°C, particularly 850-950°C, pressures of 1 to 15 bar abs., with ammonia in air concentrations of 5-15%, often about 10%, by volume.

15 The selectivity tends to increase as the space velocity is increased, and so high space velocities, greater than  $1.5 \times 10^5 \text{ h}^{-1}$ , are desirable. The space velocity depends on the linear velocity of the feed gas (at NTP) and the depth of the catalyst bed. Linear gas velocities conventionally employed in commercial atmospheric pressure ammonia oxidation processes are usually in an excess of 2000 m/h, and typically are in the range 2500-8000 m/h, preferably  
20 4000-6000 m/h. Commercial processes operating at elevated pressures tend to employ considerably higher linear gas velocities, for example 30000-40000 m/h. For economic reasons it is desirable for the bed depth to be less than 50 mm. For example with a bed of depth 20 mm, at a linear gas velocity of 4000 m/h, the space velocity is  $2 \times 10^5 \text{ h}^{-1}$ .

**Claims**

- 1 A process for the oxidation of ammonia comprising passing a mixture of ammonia and an oxygen containing gas preheated to an elevated temperature through at least one bed of a catalyst effective for the oxidation of ammonia wherein, in order to render the catalyst temperature more uniform, the gas mixture is passed through a perforate reflector disposed upstream of the catalyst bed, said reflector being effective to reflect heat radiated from the inlet face of the catalyst bed back towards the catalyst bed.
- 2 A process according to claim 1 wherein the perforations in the reflector plate comprise louvres.
- 3 A process according to claim 1 wherein the reflector comprises a pair of perforate plates having their perforations staggered with respect to one another.
- 4 A process according to any of claims 1 to 3 wherein the reflector is provided with a layer of thermal insulation on the surface thereof remote from the catalyst bed.

Fig.1.

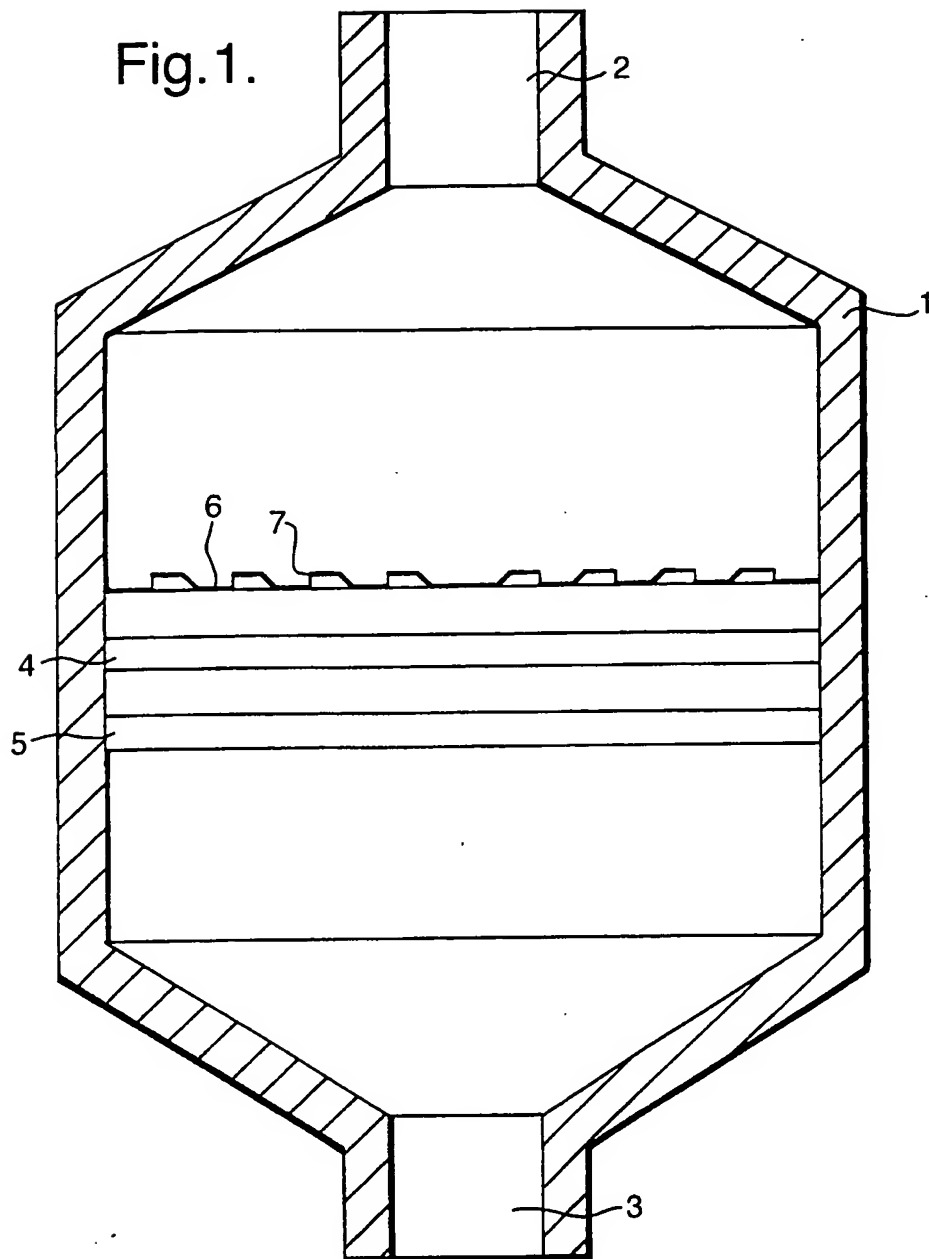
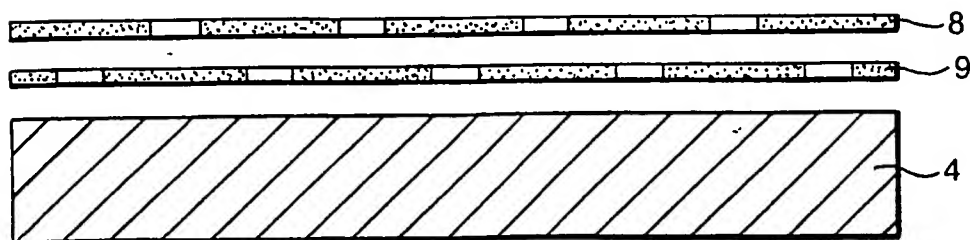


Fig.2.



# INTERNATIONAL SEARCH REPORT

In. at. Application No

PCT/GB 98/01649

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C01B21/28 B01J8/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C01B B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	B. ELVERS ET AL.: "Ullmann's Encyclopedia of industrial chemistry; vol A17, 5th Ed." 1991, VCH, WEINHEIM (DE) XP002077606 see page 307 - page 310; figures 15,17,18 ---	1
X	US 3 462 243 A (RIGA JEAN JOSEPH) 19 August 1969 see column 3, line 49 - line 59 ---	1
X	DE 37 31 988 A (STEINMUELLER GMBH L & C) 6 April 1989 see the whole document ---	1
A	US 4 170 455 A (HENRIE JAMES O) 9 October 1979 see column 5, line 52 - line 58; figure 1 ---	1
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☒ Further documents are listed in the continuation of box C.

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Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>EP 0 275 681 A (JOHNSON MATTHEY PLC)  27 July 1988</p> <p>-----</p>	

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Information on patent family members

Inventor's name Application No

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